§36. Dissipative Particle Dynamics Simulation on Self-assembly of Amphiphilic Molecules

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We studied self-assembled structure of particles with short-range interaction to compare with the long-range interaction by molecular simulation. Amphiphilic molecule was adopted as one of typical examples of particles with short-range interaction. It is known that the amphiphilic molecules have miscellaneous self-assembled structures. It is, therefore, difficult to make phase diagrams of the structure definite.

By Dissipative Particle Dynamics(DPD) simulation [1–6] which is one of "course-grained" molecular dynamics simulation methods and was developed to reveal the dynamics of a large number of particle, we obtained [7, 8] the phase diagram of a typical amphiphilic molecule, i.e. hexaoxyethylene n-dodecyl ether ($C_{12}E_6$) which is familiar to us as a nonionic surfactant.

At a room temperature, the phase diagram of $C_{12}E_6$ and water system exhibits the following phases: a hexagonal structure (H_1) are observed at 50 weight percent (50 wt %) of $C_{12}E_6$, a lamellar structure L_α at 75 wt % and so on. We showed [7,8] that the various phase structures of C12E6 are represented by the modified Jury model that is composed of one hydrophilic and one hydrophobic particle. From the simulation of the modified Jury model, we could show [7,8] H1 phase near 50 wt % and L_α phase near 75 wt %. Moreover, we showed [7,8] the dependence of phase structure on packing parameter by effectively changing the coefficients of interaction potentials among different kinds of particles.

Israelachvili proposed the packing parameter as a means of clarifying the relationship between macroscopic self-assembled structure and microscopic molecular shape [9, 10]. The packing parameter p is the ratio of the volume V occupied by the hydrophobic tail to the product of the sectional area of a hydrophilic group S and the "maximum effective length (l)" of the hydrophobic. tail The concept of the packing parameter is intuitive and acceptable. However, calculating the packing parameter is very difficult, even by computer simulation, because it is almost impossible to derive macroscopic phase structure at the microscopic level by simulation, using techniques such as molecular dynamics (MD) simulation, for example.

In order to reveal the relation between macroscopic and microscopic structure, we studied both hydrophilicity and hydrophobicity dependence of the phase structure was clarified qualitatively by varying the interaction potential among hydrophilic, hydrophobic and water molecules in a DPD simulation using the modified Jury model. By varying the coefficient of the interaction potential between hydrophilic beads, hydrophobic ones and water molecules, the effective microscopic molecule structure can be changed. The macroscopic structure, therefore, also vary according to the packing parameter of the amphiphilic molecules. In Fig. 1, we show the hydrophilicity dependence of the self-assembled structure.

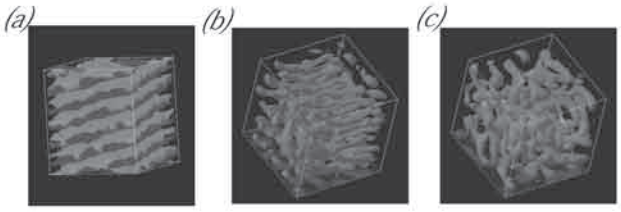

Figure 1: Self-assembly structures of amphiphilic molecule. The structure depends on the hydrophilicity of bead A and water W. We simulated three cases of the hydrophilicity coupling constant. In the most hydrophilic case(a), the amphiphilic molecures form the lamellar phase. The hexagonal and micelles phases are composed in the middle case(b) and the least case(c), respectively.

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